

1

3,109,871

PRODUCTION AND CURING OF POLYFUNCTIONAL TERMINALLY REACTIVE POLYMERS

Robert P. Zelinski, Henry L. Hsieh, and Charles W. Strobel, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware
No Drawing. Filed Dec. 27, 1960, Ser. No. 78,366
17 Claims. (Cl. 260-85.1)

This invention relates to a method of preparing and curing polyfunctional terminally reactive polymers and to the resulting products. In another aspect it relates to polymers containing terminally positioned reactive groups of two varieties which can be reacted with two entirely different types of coupling and/or curing agents.

It has been disclosed in copending application Serial No. 772,167 of Ura-neck, Short, Hsieh and Zelinski, filed November 6, 1958, that highly useful polymeric products can be obtained by polymerizing vinylidene-containing monomers in the presence of an organo alkali metal catalyst and subsequently reacting the resulting polymer containing active alkali metal end groups with a reagent which will couple the polymer molecules or replace the alkali metal with more stable reactive end groups. The utilization of these reactive terminal substituents on the polymer molecule enables substantially more effective cures since all of the molecules can be tied into the cross-linked structure. Also by simple coupling arrangements alone or with auxiliary curing, liquid polymers can be readily converted into solids and soft tacky rubber can be made quite rigid. The term "telechelic" has been coined to define these terminally reactive polymers. As used in this specification, telechelic polymers means polymers of vinylidene-containing monomers which contain a reactive group upon each end of the polymer molecule. By employing a suitable initiator, polymers can be prepared which contain reactive groups on only one end of the polymer molecule, in which case the term "semi-telechelic" is used to denote these polymers.

According to our invention a polymer is provided which contains reactive end groups of two types on at least one end of the polymer molecule. These terminally reactive polymers contain both hydroxy and tertiary amino groups which can be coupled and/or cross linked by treatment with appropriate reagents. For example, polyisocyanates react with the hydroxy groups and quaternizing agents containing 2 or more reactive halogen atoms react with the tertiary amino groups. The polyfunctional terminally reactive polymers are prepared according to our invention by reacting a polymer of a vinylidene-containing monomer, which polymer contains at least 1 terminal alkali metal atom per molecule, with either an N,N-disubstituted amino aldehyde or an N,N-disubstituted amino ketone. We have discovered that these multifunctional telechelic or semitelechelic polymers are useful not only in their ability to be cured by two different types of curing or coupling agents but also the presence of the tertiary amino group activates the cure of a polyisocyanate with the hydroxy end groups, thereby greatly improving the degree of cure possible with this type of reaction.

It is an object of our invention to provide a method of preparing polymers having polyfunctional terminally reactive groups. Another object of our invention is to provide a polymer which can be cured by two different types of coupling or curing agents reactive with hydroxy or tertiary amino groups. Another object is to provide a hydroxy-telechelic polymer which has enhanced reactivity between the hydroxy groups of the polymer and polyisocyanate curatives. Other objects and advantages and features of our invention will be apparent to those skilled in the art from the following disclosure.

2

The polymers which contain terminally reactive alkali metal atoms can be prepared from a wide variety of monomers. The preferred monomers are the conjugated dienes containing from 4 to 12 carbon atoms per molecule and preferably 4 to 8 carbon atoms per molecule. Examples of these compounds include the following: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene (piperylene), 2-methyl-3-ethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, 2-methyl-3-ethyl-1,3-pentadiene, 2-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, phenyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene and the like. Conjugated dienes containing halogen and alkoxy substituents along the chain can also be employed, such as chloroprene, fluoroprene, 2-methoxy-1,3-butadiene, 2-ethoxy-3-ethyl-1,3-butadiene, and 2-ethoxy-3-methyl-1,3-hexadiene. Conjugated dienes can be polymerized alone or in admixture with each other to form copolymers, or block copolymers. Block copolymers can be prepared from two or more conjugated dienes by charging one compound initially, allowing it to polymerize, and then adding a second conjugated diene and allowing it to polymerize. It is preferred that conjugated diolefins be employed in the practice of my invention and preferred monomers are butadiene, isoprene and piperylene.

In addition to the conjugated dienes I can practice my invention with other monomers containing a $\text{CH}_2=\text{C}<$ group such as the vinyl-substituted aromatic compounds. The vinyl-substituted aromatic compounds include styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkoxy, aryloxy, and dialkyl-amino derivatives thereof in which the total number of carbon atoms in the combined substituents is generally not greater than 12. Examples of these aromatic monomers include: 3-methylstyrene (3-vinyltoluene), 3,5-diethylstyrene, 4-n-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 3-methyl-5-n-hexylstyrene, 4-cyclohexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 3,5-diphenylstyrene, 2,4,6-tri-tert-butylstyrene, 2,3,4,5-tetramethylstyrene, 4-(4-phenyl-n-butyl)styrene, 3-(4-n-hexylphenyl)styrene, 4-methoxystyrene, 3,5-diphenoxystyrene, 3-decoxystyrene, 2,6-dimethyl-4-hexoxystyrene, 4-dimethylaminostyrene, 3,5-diethylaminostyrene, 4-methoxy-6-di-n-propylaminostyrene, 4,5-dimethyl-1-vinylnaphthalene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 2,4-diisopropyl-1-vinylnaphthalene, 3,6-di-p-tolyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 4,5-diethyl-8-octyl-1-vinylnaphthalene, 3,4,5,6-tetramethyl-1-vinylnaphthalene, 3,6-di-n-hexyl-1-vinylnaphthalene, 8-phenyl-1-vinylnaphthalene, 5-(2,4,6-trimethylphenyl)-1-vinylnaphthalene, 3,6-diethyl-2-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene, 4-n-propyl-5-n-butyl-2-vinylnaphthalene, 6-benzyl-2-vinylnaphthalene, 3-methyl-5,6-diethyl-8-n-propyl-2-vinylnaphthalene, 4-o-tolyl-2-vinylnaphthalene, 5-(3-phenyl-n-propyl)-2-vinylnaphthalene, 4-methoxy-1-vinylnaphthalene, 6-phenoxy-1-vinylnaphthalene, 3,6-dimethylamino-1-vinylnaphthalene, 7-dihexoxy-2-vinylnaphthalene and the like. These vinyl-substituted aromatic compounds can be used to form copolymers including block copolymers with conjugated dienes. The presence of a small amount of polar compound such as the solvent used in preparing the initiator encourages random copolymerization between conjugated dienes and the vinyl-substituted aromatic compounds.

Certain polar monomers can also be polymerized to form copolymers. These polar monomers can be employed to form block copolymers with conjugated dienes.